



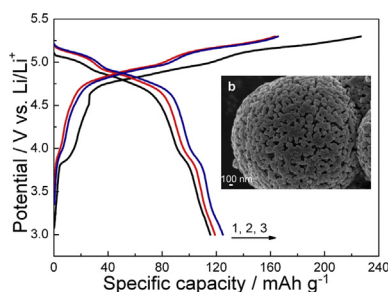
Short communication

Porous hollow LiCoMnO_4 microspheres as cathode materials for 5 V lithium ion batteriesMeng Hu^a, Yuan Tian^a, Jinping Wei^a, Dengguo Wang^b, Zhen Zhou^{a,*}^a Tianjin Key Laboratory of Metal and Molecule Based Material Chemistry, Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Institute of New Energy Material Chemistry, Synergetic Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, China^b KST Battery Material Company, Gaoyao, Guangdong 526100, China

HIGHLIGHTS

- Porous hollow LiCoMnO_4 microspheres were prepared for 5 V lithium ion batteries.
- LiCoMnO_4 microspheres combined porous structures in the surface and hollow structures inward.
- LiCoMnO_4 microspheres exhibited high capacity, good cyclic reversibility and rate capability.

GRAPHICAL ABSTRACT



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ABSTRACT

Porous hollow LiCoMnO_4 microspheres have been prepared and tested as cathode materials for 5 V lithium ion batteries. The microspheres, which combine porous structures in the surface and hollow structures inward, show high capacity, good cyclic reversibility and rate capability as cathode materials for high-voltage Li ion batteries. The LiCoMnO_4 microspheres exhibit an initial discharge capacity of 115.5 mAh g^{-1} at 1 C, maintain a discharge capacity of 91.7 mAh g^{-1} after 60 cycles with the capacity retention of 79.4%. When cycled at 5 C, the initial capacity is 95.5 mAh g^{-1} , and the capacity retention is 52.6% after 60 cycles. The special porous hollow structure allows for the full contact with the electrolyte, enhances the electrochemical reaction kinetics, and buffers the volume expansion thus maintaining the structural integrity.

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1. Introduction

There are great challenges to develop lithium ion batteries with high energy and power density for electric vehicles and hybrid electric vehicles [1]. The spinel LiMn_2O_4 is an extensively studied

cathode material due to low cost, good electrochemical performance and high thermal stability. However, its energy density is not high. Partly substituting transition metals with higher potential couples for Mn could increase the discharge plateaus, and the energy density accordingly [2]. Among the various doping derivatives, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is a promising material, which exhibits a flat discharge plateau around 4.7 V vs. Li/Li^+ and provides 18% higher energy density than LiMn_2O_4 . Compared with $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, the Co doping derivative LiCoMnO_4 with the $\text{Co}^{3+}/\text{Co}^{4+}$ redox couple

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delivers higher potential at ~ 5.0 V vs. Li/Li^+ [3,4]. Considering similar theoretical specific capacity but higher redox potential, one may expect that LiCoMnO_4 can provide even higher energy density than $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

LiCoMnO_4 was first reported by Kawai et al. in 1998 [5]. The previous studies mainly focused on the structural transitions under high temperatures [6–9]. The oxygen deficiency was observed above 600°C accompanied with the reversible transformation from spinel to rock salt, and the Mn^{4+} ions in $\text{LiCoMnO}_{4-\delta}$ were partially reduced to Mn^{3+} [7,10]. However, the studies on the electrochemical performance and the morphology control of LiCoMnO_4 are rather limited. LiCoMnO_4 cathode materials prepared through direct solid state reactions or sol–gel methods tend to agglomerate into large particles, which hinder the Li^+ diffusion. Recently, hollow structures have been proposed to cushion the volume expansion and facilitates the Li^+ diffusion. Various hollow anode materials (transition metal oxides and sulfides) and cathode materials (LiMn_2O_4 , $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, LiVOPO_4 , etc.) have been reported and exhibited excellent electrochemical performances [11–21]. Nevertheless, the solid surfaces of hollow spheres may inhibit the electrolyte infiltration. Building porous structures in the surfaces of hollow spheres would overcome the problem.

Herein, we prepared porous hollow LiCoMnO_4 microspheres combining porous structures in the surface and hollow structures inward, and used them as cathode materials for 5 V lithium ion batteries, which exhibited good cyclic stability and rate capability.

2. Experimental

2.1. Material preparation

To obtain porous hollow LiCoMnO_4 microspheres, $\text{Co}_{0.5}\text{Mn}_{0.5}\text{CO}_3$ microspheres were synthesized firstly. 1.5 m mol $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, 1.5 m mol $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, and 21 mL ethanol were dissolved in 210 mL deionized water with magnetic agitation. Also, 30 m mol NH_4HCO_3 was dissolved in 210 mL deionized water, and then the NH_4HCO_3 solution was added to the above CoSO_4 and MnSO_4 system with agitation. The mixed solution was maintained for 3 h at room temperature and then centrifuged. The precipitate was separated and washed with water and ethanol. The as-prepared $\text{Co}_{0.5}\text{Mn}_{0.5}\text{CO}_3$ microspheres were dried at 60°C to remove the solvent. 1 m mol $\text{Co}_{0.5}\text{Mn}_{0.5}\text{CO}_3$ and 0.525 m mol $\text{LiOH} \cdot \text{H}_2\text{O}$ were dispersed in 5 mL ethanol under agitation. After the ethanol was evaporated, the mixture was calcined at 800°C for 20 h in air.

2.2. Material characterization

X-ray diffraction (XRD) was performed on a D/MAX III diffractometer with $\text{Cu K}\alpha$ radiation. Field emission scanning electron microscope (FESEM) images were obtained on a JEOL-JSM7500 microscope. The energy dispersive X-ray spectroscopy (EDX) attached to the FESEM instrument was used to confirm the composition of the samples. Transmission electron microscope (TEM) images were taken on a FEI Tecnai G²F-20 field emission TEM.

2.3. Electrochemical tests

The working electrode was composed of active material, acetylene black, and polyvinylidene fluoride (PVDF) binder with a weight ratio of 80:10:10. The above powders were mixed and dispersed in *N*-methyl-2-pyrrolidone, and the obtained slurry was coated onto Al foil. The diameter of the cathode films was 12 mm, and the loading mass of the cathodes was ~ 1.5 mg. The electrolyte was 1 M LiPF_6 dissolved in a mixture of ethylene carbonate (EC),

ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC) (1:1:1 by volume, Tianjin Jinniu Power Source Material Co., Ltd.). The Li//LiCoMnO_4 CR2025-type coin cells were assembled in an argon-filled glove box. Galvanostatic charge/discharge tests were performed on a Land CT2001 battery tester between 3.0 and 5.3 V at 25°C . Cyclic voltammograms (CVs) were performed on a CHI600A electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd.) in a potential range of 3.0–5.3 V at a scan rate of 0.1 mV s^{-1} .

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-prepared $\text{Co}_{0.5}\text{Mn}_{0.5}\text{CO}_3$ precursor and LiCoMnO_4 . The diffraction peaks of $\text{Co}_{0.5}\text{Mn}_{0.5}\text{CO}_3$ are well consistent with MnCO_3 (JCPDS#83-1763), and the peaks integrally shift to larger angles due to the smaller radius of Co^{2+} compared with Mn^{2+} . The diffraction peaks of LiCoMnO_4 are indexed to the spinel structure with the space group of $Fd\bar{3}m$ and consistent with the previous studies [7,22]. The slight impurity might be some lithium manganese oxides.

The SEM image and the EDX spectrum of $\text{Co}_{0.5}\text{Mn}_{0.5}\text{CO}_3$ are shown in Fig. 2. According to the EDX spectrum, the Mn/Ni atomic ratio in the $\text{Co}_{0.5}\text{Mn}_{0.5}\text{CO}_3$ spheres is 1:1. From the SEM images of the LiCoMnO_4 samples in Fig. 3, we can see that the LiCoMnO_4 samples are composed of microspheres with the diameters of about 2–4 μm , similar to the $\text{Co}_{0.5}\text{Mn}_{0.5}\text{CO}_3$ spheres. As shown in Fig. 3b, the surfaces of the spheres are porous and constructed with submicron-sized particles. The sphere interior is highly vacant (Fig. 3c). From the TEM image in Fig. 3d, the light periphery indicates the porous structure of the surface. The light contrast of the interiors confirms the hollow structure. The formation of the hollow structures is attributed to the decomposition of the carbonate precursors as well as the fast outward diffusion of Mn and Co and the slow inward diffusion of O [23]. In addition, the decomposition of the carbonates and the volume change are responsible for the porous surfaces.

The electrochemical performances of the as-prepared porous hollow LiCoMnO_4 microspheres were studied subsequently. The CV curves are shown in Fig. 4a. Four pairs of anodic and cathodic peaks are clearly observed. The two pairs of peaks around 5 V come from the $\text{Co}^{3+}/\text{Co}^{4+}$ couples, indicating the Li^+ ordering in tetrahedral sites and the two-step extraction/insertion [24]. The peaks around 4 V are attributed to the $\text{Mn}^{3+}/\text{Mn}^{4+}$ couple. The Mn^{3+} ions are generated by the part reduction of Mn^{4+} accompanied with oxygen

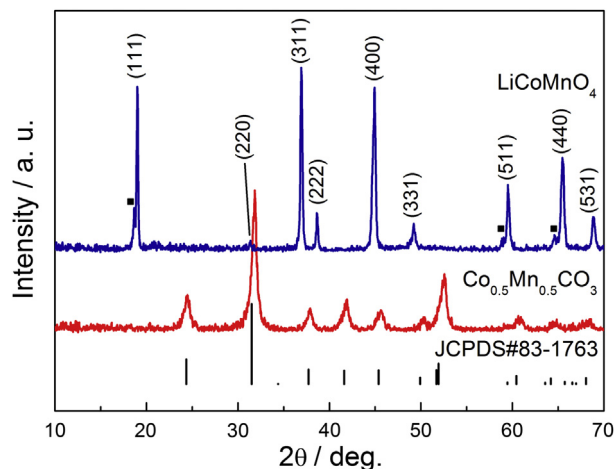


Fig. 1. XRD patterns of the as-prepared $\text{Co}_{0.5}\text{Mn}_{0.5}\text{CO}_3$ and LiCoMnO_4 samples (■ impurity).

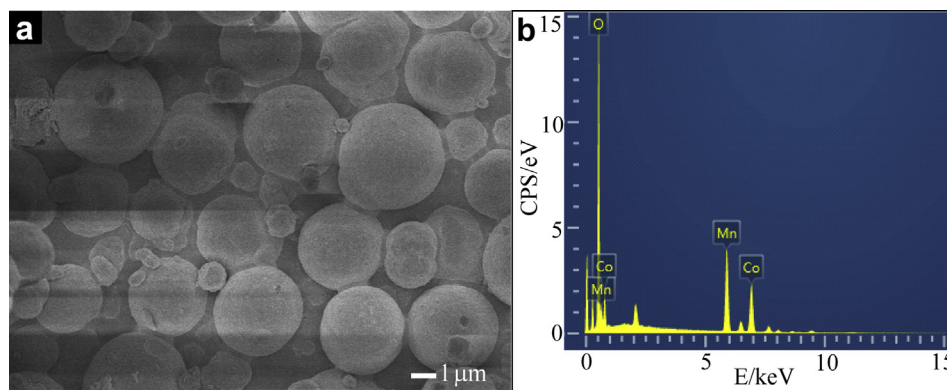


Fig. 2. SEM image (a) and EDX spectrum (b) of the as-prepared $\text{Co}_{0.5}\text{Mn}_{0.5}\text{CO}_3$ sample.

deficiency under elevated temperatures during the preparation process. The minor peaks at ~ 3.2 V may be attributed to the structural transition of the material. After the first cycle, the differences between the anodic peaks and the corresponding cathodic peaks decrease distinctly, demonstrating the decreased polarization after the activation of the electrode and the infiltration of the electrolyte into the porous hollow structures. The galvanostatic charge/discharge curves of the initial three cycles are shown in Fig. 4b, at a rate of 1 C (145 mA g^{-1}). The plateaus are well consistent with the CV curves, and the average discharge potentials of the $\text{Co}^{3+}/\text{Co}^{4+}$ couples are ~ 4.9 V, which are higher than those of the $\text{Ni}^{2+}/\text{Ni}^{4+}$ couples. The initial charge capacity exceeds the theoretical value due to the decomposition of the electrolyte under high potentials. The discharge capacity is 115.5 mAh g^{-1} , and the capacities increase in the following cycles after the electrolyte

infiltration and the activation of the electrodes. When the test rate increases from 0.1 to 1, 2, and 5 C (Fig. 4c), the discharge capacities are 123.0, 115.5, 96.5, and 95.5 mAh g^{-1} , respectively. The discharge plateaus at 5 C were lowered obviously due to the rapid tests, which are unfavorable for the electrolyte infiltration and the Li^+ diffusion kinetics, and the discharge plateaus were recovered to ~ 4.9 V in the following cycles, which approached to the values at other rates. The cyclic performance of the porous hollow LiCoMnO_4 microspheres is shown in Fig. 4d. After 60 cycles at 1 C, the discharge capacity is 91.7 mAh g^{-1} , and the capacity retention is 79.4%. When cycled at 5 C, the capacity decreases to 50.2 mAh g^{-1} , retaining 52.6% of the initial capacity after 60 cycles. The Coulombic efficiency of the electrodes at 1 C is around 80% (Fig. 4d) due to the decomposition of electrolytes at high potentials. The LiCoMnO_4 cathodes were observed after 60 charge/discharge cycles at 1 C, and

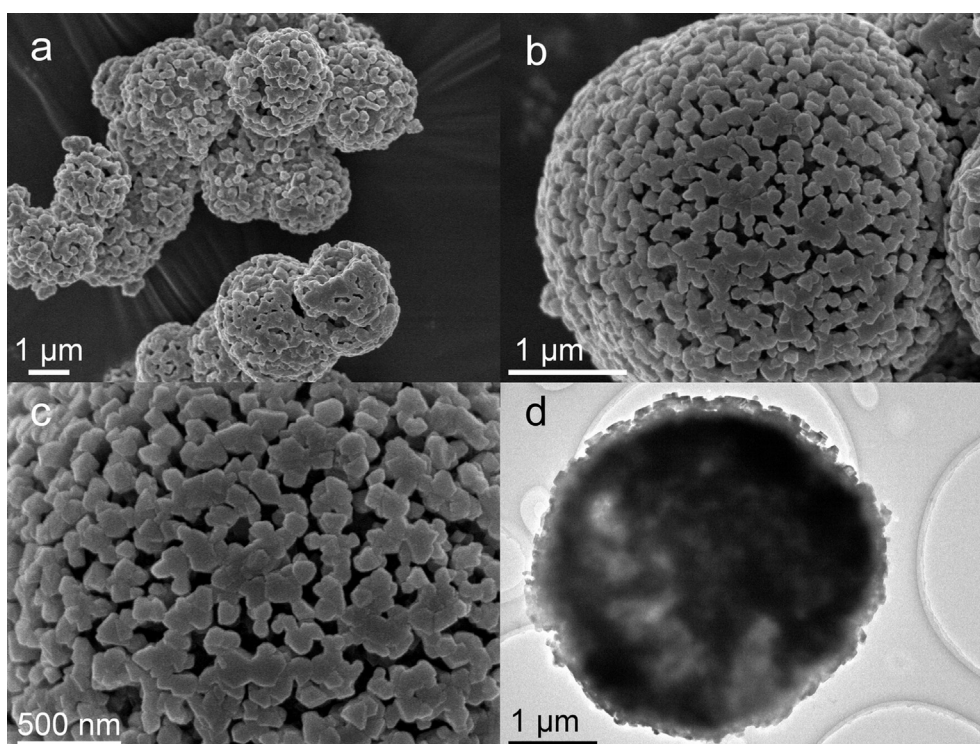


Fig. 3. SEM (a,b,c) and TEM (d) images of the porous hollow LiCoMnO_4 spheres.

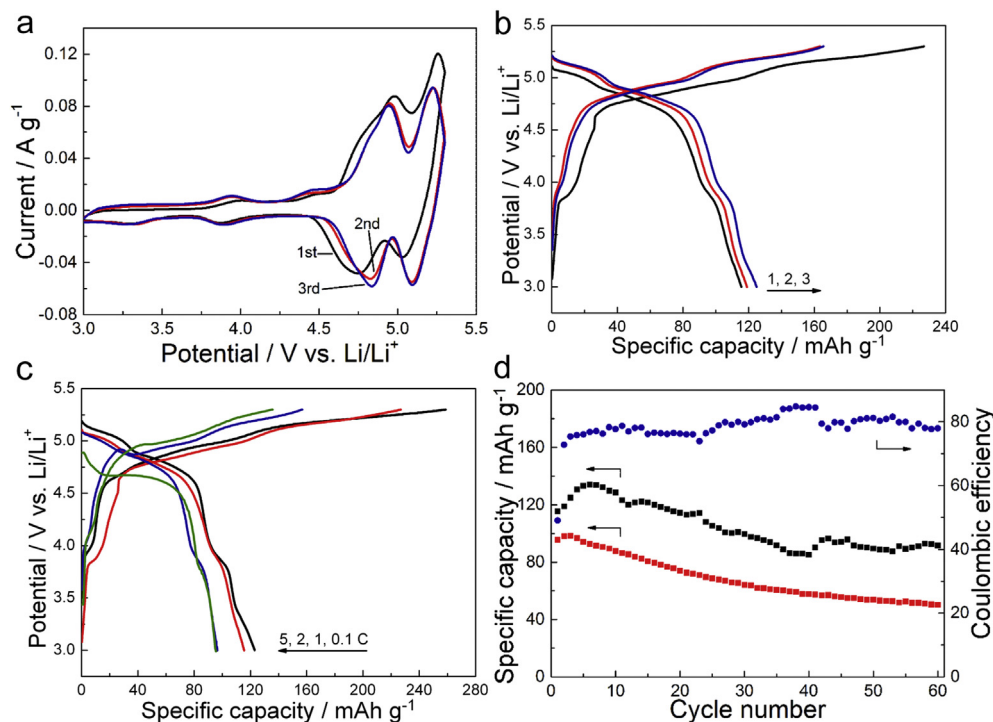


Fig. 4. (a) CV curves, (b) charge/discharge curves at 1 C for the initial three cycles, (c) charge/discharge curves at different rates, and (d) cyclic performance at 1 C and 5 C, and Coulombic efficiency at 1 C of the porous hollow LiCoMnO₄ spheres.

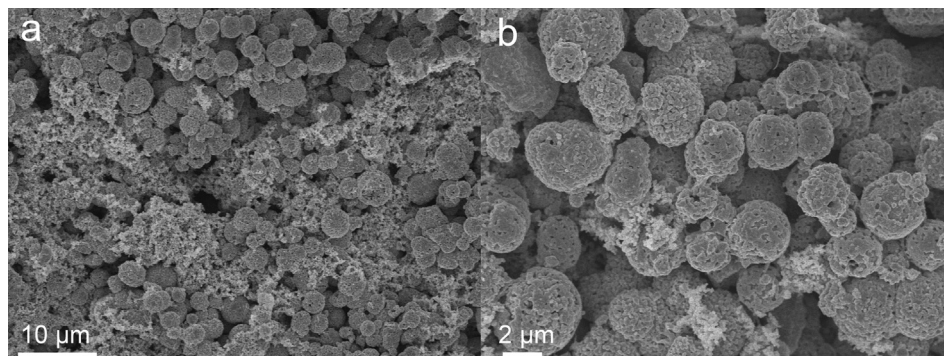


Fig. 5. SEM images of the porous hollow LiCoMnO₄ cathodes after 60 charge/discharge cycles at 1 C.

the SEM images are shown in Fig. 5. The morphology of porous hollow microspheres was well maintained for LiCoMnO₄ cathodes after 60 cycles. The small particles around the microspheres are acetylene black. The porous hollow microspheres are stable under repetitive Li intercalation/deintercalation procedures. Compared with the previous studies [5,22,25,26], the hollow LiCoMnO₄ microspheres exhibited both higher capacity and better cyclic stability.

The excellent electrochemical performances of LiCoMnO₄ cathode materials are attributed to the peculiar structures. The nano-sized particles and the porous structures reduce Li⁺ diffusion length and improve the ionic diffusion. The hollow structures allow for the full contact of the particles with the electrolyte and enhance the electrochemical reaction kinetics. In addition, the porous hollow structures buffer the volume expansion and maintain the structural integrity. With high discharge plateaus, LiCoMnO₄ is a candidate cathode material for 5 V lithium ion batteries. Compared with the well studied LiNi_{0.5}Mn_{1.5}O₄, LiCoMnO₄ exhibits even

higher electrode potential and delivers higher energy density accordingly. Nevertheless, the cyclic performances of LiCoMnO₄ are still inferior to LiNi_{0.5}Mn_{1.5}O₄ at the current stage due to the higher charge potentials; therefore, the optimization of the electrolyte is also essential in the future studies.

4. Conclusion

In summary, porous hollow LiCoMnO₄ microspheres were prepared and tested as cathode materials for 5 V lithium ion batteries, which combine porous structures in the surface and hollow structures inward. The LiCoMnO₄ microspheres exhibited initial discharge capacities of 115.5 mAh g⁻¹ at 1 C and 95.5 mAh g⁻¹ at 5 C, and the capacity retention was 79.4% and 52.6% after 60 cycles, respectively. The special porous hollow structure endows LiCoMnO₄ promising cathode materials for 5 V lithium ion batteries, with aid of the future development of high-voltage electrolytes.

Acknowledgments

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